

Second Annual Progress Report  
For the Project

**Flow Tube Studies of Gas Phase Chemical Processes  
of Atmospheric Importance**

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# Flow Tube Studies of Gas Phase Chemical Processes of Atmospheric Importance

## Objective:

The objective of this project is to conduct measurements of elementary reaction rate constants and photochemical parameters for processes of importance in the atmosphere. These measurements are being carried out under temperature and pressure conditions covering those applicable to the stratosphere and upper troposphere, using the chemical ionization mass spectrometry turbulent flow technique developed in our laboratory.

The next section summarizes our research activities during the first year of the project, and the section that follows consists of the statement of work for the third year. Additional details concerning the projects listed in the statement of work were described in our original proposal.

## Accomplishments:

### Production of HCl in the OH + ClO Reaction

We have continued our investigations of the OH + HCl reaction, focussing on the branching ratio for HCl formation:



Early attempts to measure the branching ratio were unable to rule out an HCl yield of zero for the minor channel 1b due to uncertainties in the experimental data [Leu & Lin, 1979; Burrows *et al.*, 1984; Hills & Howard, 1984; Poulet *et al.*, 1986]. As a result, no consensus had been reached on the atmospheric significance of this channel. As detailed in our previous progress report, we conducted the first direct measurement of a product from reaction 1b [Lipson *et al.*, 1997]. In those branching ratio experiments, OD was used instead of OH due to the large HCl background produced by the

ClO source. Since there was virtually no DCl background, we were able to observe production of very small concentrations of DCl ( $\sim 10^9$  molecule  $\text{cm}^{-3}$ ) over the experimental reaction time that we positively identified as coming from the minor channel of the OD + ClO reaction. The branching ratio ( $k_{1b}/k_1$ ) was determined to be  $0.05 \pm 0.02$  at 298 K and  $0.06 \pm 0.02$  at 210 K.

Because of the demonstrated atmospheric importance of reaction 1b and because of the possibility of an isotope effect, we decided to conduct branching ratio measurements for the OH + ClO reaction. Recent improvements in our experimental technique have led to significantly reduced HCl background in our system, thus making it possible to observe the production of very small concentrations of HCl ( $\sim 10^9$  molecule  $\text{cm}^{-3}$ ). In this progress report we summarize the results of our investigation of the branching ratio of reaction 1. The measurements were conducted at pressures between 100 and 200 Torr and over a range of temperatures extending to those found in the lower stratosphere; as before, we used a turbulent flow tube coupled to a high-pressure chemical ionization mass spectrometer.

Several critical changes to the method of ClO production have greatly reduced the HCl background in the system. The flow tube (2.2-cm i.d., 120 cm long) was constructed of Pyrex tubing and coated with Halocarbon wax. A large flow of nitrogen carrier gas (40-75 STP liter  $\text{min}^{-1}$ ) was injected at the rear of the flow tube. The gases needed to generate OH were introduced through a sidearm (12 cm long, 6 mm diameter) located at the rear of the flow tube. ClO was generated in a double nested movable injector that consisted of an inner 6-mm alumina tube and an outer encasement made from corrugated Teflon tubing. The outer encasement was used so that the injector could be moved to various positions without breaking any vacuum seals, as well as to prevent ambient gases from condensing on cold portions of the injector. A Teflon device (described below) was placed at the end of the injector in order to enhance turbulent mixing. The electric discharge ion source was located between the temperature regulated flow tube and the inlet to the quadrupole mass spectrometer. A variable-sized aperture (1.2-1.8 mm diameter) was used to create a pressure drop between the flow tube and the ion-molecule region. The size of the aperture was adjusted so that the pressure in the ion-molecule region remained roughly constant at 15 Torr while the pressure in the flow tube was varied between 100 and 200 Torr.

We also made several important modifications to the ClO generation system to reduce the HCl background in the flow tube by more than an order of magnitude. In our previous study of the branching ratio, the high HCl background ( $\sim 10^{11}$  molecule  $\text{cm}^{-3}$ ) in the system was coming primarily from the ClO source. This large background made it difficult to detect small amounts of HCl produced by reaction 1b over the experimental reaction time. We have determined that a significant portion of the HCl background was coming from trace impurities of  $\text{H}_2$  in the helium sweep gas used to flush  $\text{Cl}_2$  through the microwave discharge. Although 99.999% pure helium was used, the manufacturer specifications indicate levels of  $\text{H}_2$  up to 1 ppm. If 1 ppm of  $\text{H}_2$  ( $\sim 10^{12}$  molecule  $\text{cm}^{-3}$ ) were present and passed through the microwave discharge in the presence of chlorine, enough H atoms to create a sizable HCl background could have been produced. This source of HCl was significantly reduced by installing an Aeronex inert gas purifier that removes  $\text{H}_2$  impurities to sub-ppb levels. In addition to using the purifier, we have also changed the sweep gas through the chlorine microwave discharge from helium to argon. Argon increases the efficiency of  $\text{Cl}_2$  microwave dissociation, making it possible to produce the same amount of ClO using less  $\text{Cl}_2$ . Even the UHP grade  $\text{Cl}_2$  (>99.9% pure) used in this study contains small amounts of HCl impurities. Despite attempts to further purify the UHP grade gas, the  $\text{Cl}_2$  remained a small source of HCl background in our experiments. However, switching to an argon sweep gas made it possible to use lower initial  $\text{Cl}_2$  concentrations, and thereby helped to reduce the HCl background in the system. Finally, another significant source of HCl background was identified as coming from the interaction of Cl atoms with the glass walls of the movable injector (particularly in the few centimeters after the chlorine microwave discharge, but before the introduction of excess  $\text{O}_3$ ). This contribution to the HCl background was significantly reduced by switching to an injector made out of alumina. Overall, modifications to the ClO source have reduced the HCl background in the system by more than an order of magnitude (from  $\sim 10^{11}$  to  $\sim 10^{10}$  molecule  $\text{cm}^{-3}$ ), making it possible to observe production of very small amounts of HCl from reaction 1b. Decreasing the HCl background was critical to our ability to make accurate measurements of the branching ratio for the  $\text{OH} + \text{ClO}$  reaction.

In addition to the sources of HCl mentioned above, the production of HCl background by secondary reactions in the main flow tube was also a concern. For example, the products of the main channel of the OH + ClO reaction are HO<sub>2</sub> and Cl. Unfortunately, HO<sub>2</sub> and Cl can react further to form HCl ( $k_3 = 3.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) [DeMore *et al.*, 1997]:



Since reaction 3 is relatively fast, and HO<sub>2</sub> and Cl are the major products of the OH + ClO reaction, reaction 3 was found to be the largest potential source of HCl background due to secondary chemistry. However, the large excess of O<sub>3</sub> ( $\sim 10^{13} \text{ molecule cm}^{-3}$ ) used in the production of ClO also helped to scavenge Cl atoms produced by reaction 1a, and therefore, helped to minimize HCl background production from side reactions such as reaction 2.

With these improvements, we were able to observe production of very small concentrations of HCl ( $\sim 10^9 \text{ molecule cm}^{-3}$ ) over the reaction time ( $\sim 20 \text{ ms}$ ) which we have positively identified as coming from reaction 1b. The rise of HCl could easily be observed above the background noise. Under the optimal experimental conditions ( $[\text{ClO}] \sim 1 \times 10^{12} \text{ molecule cm}^{-3}$  and  $[\text{OH}] \sim 1 \times 10^{11} \text{ molecule cm}^{-3}$ ), modeling shows that side reactions can only produce concentrations of HCl that are less than the detection limit of our instrument ( $\sim 2 \times 10^8 \text{ molecule cm}^{-3}$ ). Table 1 contains a list of the reactions used in the modeling. The following side reactions can produce HCl in our system:



**Table 1.** Chemical Reactions Used in Computer Simulations for the Branching Ratio Studies

Reaction	k <sup>a</sup> (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
OH + ClO → HO <sub>2</sub> + Cl	1.46 x 10 <sup>-11</sup>
OH + ClO → HCl + O <sub>2</sub>	see text
Cl + HO <sub>2</sub> → HCl + O <sub>2</sub>	3.2 x 10 <sup>-11</sup>
Cl + HO <sub>2</sub> → OH + ClO	9.1 x 10 <sup>-12</sup>
Cl + O <sub>3</sub> → ClO + O <sub>2</sub>	1.2 x 10 <sup>-11</sup>
Cl + H <sub>2</sub> → HCl + H	1.6 x 10 <sup>-14</sup>
Cl + NO <sub>2</sub> + M → ClONO + M	3.3 x 10 <sup>-12</sup>
H + Cl <sub>2</sub> → HCl + Cl	2.5 x 10 <sup>-11</sup>
H + O <sub>3</sub> → OH + O <sub>2</sub>	2.9 x 10 <sup>-11</sup>
H + NO <sub>2</sub> → OH + NO	1.3 x 10 <sup>-10</sup>
OH + O <sub>3</sub> → HO <sub>2</sub> + O <sub>2</sub>	6.8 x 10 <sup>-14</sup>
OH + Cl <sub>2</sub> → HOCl + Cl	6.7 x 10 <sup>-14</sup>
OH + OH → H <sub>2</sub> O + O	1.9 x 10 <sup>-12</sup>
OH + OH + M → H <sub>2</sub> O <sub>2</sub> + M	1.4 x 10 <sup>-12</sup>
OH + HO <sub>2</sub> → H <sub>2</sub> O + O <sub>2</sub>	1.1 x 10 <sup>-10</sup>
OH + NO <sub>2</sub> + M → HNO <sub>3</sub> + M	3.3 x 10 <sup>-12</sup>
OH + NO + M → HONO + M	1.7 x 10 <sup>-12</sup>
OH + HCl → H <sub>2</sub> O + Cl	8.0 x 10 <sup>-13</sup>
ClO + ClO → products	7.7 x 10 <sup>-14</sup>
ClO + HO <sub>2</sub> → HOCl + O <sub>2</sub>	5.0 x 10 <sup>-12</sup>
ClO + NO → NO <sub>2</sub> + Cl	1.7 x 10 <sup>-11</sup>
ClO + NO <sub>2</sub> + M → ClONO <sub>2</sub> + M	4.6 x 10 <sup>-13</sup>
HO <sub>2</sub> + HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	1.9 x 10 <sup>-12</sup>
HO <sub>2</sub> + NO <sub>2</sub> + M → HO <sub>2</sub> NO <sub>2</sub> + M	3.8 x 10 <sup>-13</sup>
HO <sub>2</sub> + NO → NO <sub>2</sub> + OH	8.1 x 10 <sup>-12</sup>

<sup>a</sup>Rate constants are from ref. 1, ref. 29 and ref. 31, at 298 K and 100 Torr

In our experiments, the source conditions for OH and ClO are optimized in order to prevent stray H and Cl atoms from entering the main flow tube. Modeling of the OH source shows that the concentration of H atoms is so small that reaction 3 is negligible as a source of HCl production. Furthermore, reaction 4 is too slow to be important in our reaction system ( $k_{13} = 1.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) [Mallard *et al.*, 1994]. Reactions 3 and 4 combine to produce HCl concentrations far below the detection limit of the instrument. Reaction 2 is more difficult to avoid because HO<sub>2</sub> and Cl are the products of reaction 1a, the main channel of the OH + ClO reaction. However, modeling shows that the large excess of O<sub>3</sub> — used to generate ClO — is efficient in scavenging Cl atoms produced in the main flow tube. Under optimal experimental conditions, reaction 2 can only produce levels of HCl ( $\sim 10^8 \text{ molecule cm}^{-3}$ ) that are below the detection limit of the instrument.

Although modeling shows that for optimal initial conditions the observed HCl production cannot be due to homogeneous side reactions, the possibility exists that the HCl could be a result of heterogeneous reactions on the wall of the flow tube. In our previous study of OD + ClO [Lipson *et al.*, 1997], we performed two control experiments to demonstrate that the observed DCl production was not due to heterogeneous processes. First, we checked that an uncoated tube gave results in very good agreement with those obtained with the Halocarbon wax-coated tube, indicating that the observed DCl production was not due to reactions on the wall of the flow tube. Second, the total pressure in the flow tube was increased by almost a factor of two; the effects of heterogeneous processes are reduced at higher pressures [Seeley *et al.*, 1993], and yet the branching ratio did not decrease, providing further evidence that the observed DCl production was not due to heterogeneous processes. In fact, the branching ratio for OD + ClO was observed to increase by  $\sim 35\%$  at the higher pressure (180 vs. 95 Torr). Considering experimental uncertainties, we were not able to draw any definite conclusions about the pressure dependence of the branching ratio at that time. There are many examples of radical-radical reactions that proceed through an intermediate complex, which is stabilized at higher pressures. However, in the case of OD + ClO, theoretical calculations indicate that the intermediate complex (DOOCl\*) is not long-lived enough to be pressure stabilized under atmospheric conditions [Dubey *et al.*, 1998].

**Table 2.** Summary of Experimental Conditions and Results for the Branching Ratio Studies of the OH + ClO Reaction

Expt. No.	T (K)	P (Torr)	[OH] <sub>0</sub> (10 <sup>11</sup> molec cm <sup>-3</sup> )	[ClO] <sub>0</sub> (10 <sup>11</sup> molec cm <sup>-3</sup> )	k <sub>1b</sub> (10 <sup>-13</sup> cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	branching ratio (k <sub>1b</sub> /k <sub>1</sub> )
1	298	98	3.5	6.0	10.2	0.070
2	298	94	2.2	6.1	9.5	0.065
3	298	97	1.8	8.3	10.4	0.071
4	298	96	1.4	7.9	8.6	0.059
5	298	96	1.9	4.9	10.2	0.070
6	298	94	1.2	8.2	9.1	0.062
7	298	191	2.2	7.0	8.3	0.057
8	298	201	1.3	5.7	9.1	0.062
9	298	203	1.9	6.6	10.2	0.070
10	275	171	2.2	6.9	10.2	0.064
11	259	152	1.5	5.8	10.5	0.062
12	246	157	1.4	6.2	12.2	0.068
13	233	152	1.8	5.6	13.1	0.068
14	217	140	1.7	6.6	15.1	0.071
15	207	127	2.5	6.5	14.5	0.064

In the present study, we have conducted a more thorough investigation of the pressure dependence of the OH + ClO branching ratio, and the results are presented in Table 2. The measured rate constants for the minor channel at 200 Torr are clearly within the range of the values for the 100 Torr experiments. In these experiments we saw no evidence for a pressure effect on the rate constant of reaction 1b. Furthermore, in our previous work [Lipson *et al.*, 1997], the overall rate constant of the OH + ClO reaction (k<sub>1</sub>) was found to be independent of pressure as demonstrated by the good agreement between our measurements at 100 Torr and previous measurements at low pressure (~1 Torr) [Hills & Howard, 1984]. As a result, we conclude that the branching ratio of the OH + ClO reaction is independent of pressure under conditions relevant to the atmosphere. Two important modifications to the experimental apparatus have been made for these



measurements, which might help to explain the small apparent pressure effect in the DCI experiments: (1) the diameter of the aperture between the flow tube and ion-molecule region was varied in order to maintain a constant pressure in the ion-molecule region for the HCl measurements at 200 Torr. In the DCI experiments, the aperture size was kept constant even at higher pressures. Thus, the doubling of pressure in the flow tube from 95 to 180 Torr also created a doubling of pressure in the ion-molecule region. This doubling of neutral concentrations in the ion-molecule region may have contributed to an increase in secondary ion-molecule reactions which could have affected the DCI experiments at 180 Torr; and (2) the shape of the Teflon device, at the end of the movable injector, was redesigned to better enhance turbulent mixing in the flow tube at increased pressures. In our DCI experiments, an open, fan-shaped device (a turbulizer) was used for the measurements at both 95 and 180 Torr. In the new design, the gas in the movable injector is forced through a series of small holes punched in several pieces of Teflon tubing that protrude into the flow tube perpendicular to the direction of the main flow; experimental tests have shown improved mixing at 200 Torr. The entire branching ratio studies for the OH + ClO reaction were conducted using this improved turbulizer design. Thus, in the DCI experiments at 180 Torr, insufficient mixing may have contributed to the error in the measurement of the branching ratio. Overall, the discrepancy between the HCl and DCI measurements at increased pressures is certainly within the reported errors of the measurements. However, we believe that these two recent improvements to the apparatus have produced more accurate measurements of the branching ratio for the OH + ClO reaction at 200 Torr.

We performed several measurements of the branching ratio for OH + ClO at temperatures between 207 and 298 K in order to establish the temperature dependence of the rate constant  $k_{1b}$  under conditions relevant to the stratosphere. From the data listed in Table 2, we obtain the Arrhenius expression  $k_{1b}(T) = (3.2 \pm 0.8) \times 10^{-13} \exp [(325 \pm 60) / T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The uncertainty represents the two standard deviation statistical error in the data and is not an estimate of systematic errors. The negative temperature dependence of  $k_{1b}$  indicates that reaction 1b goes through an intermediate complex [Kaye, 1987; Troe, 1994]. The branching ratios ( $k_{1b}/k_1$ ) reported in Table 2 were calculated using the measured Arrhenius expression for the overall rate constant of the OH + ClO reaction from our previous publication ( $k_1(T) = (5.5 \pm 1.6)$

$\times 10^{-12} \exp[(292 \pm 72)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) [Lipson *et al.*, 1997]. The branching ratio for the OH + ClO reaction has been determined to be  $0.07 \pm 0.03$ , and within the error of the measurement, the branching ratio does not appear to have a very strong temperature dependence. The reported error for the branching ratio is an estimate of the systematic error and the uncertainty of the model fitting procedure based on a sensitivity analysis. In our previous studies of the OD + ClO reaction [Lipson *et al.*, 1997], we found that the branching ratio to form DCl ranged from  $0.05 \pm 0.02$  at 298 K to  $0.06 \pm 0.02$  at 210 K. In the OH + ClO branching ratio studies at low temperatures, there may exist a slight trend toward increasing branching ratios at colder temperatures. However, within the error of the OH + ClO branching ratio measurements, it is difficult to positively identify a trend of less than 1%. As a result, we conclude that the branching ratio is essentially independent of temperature under conditions relevant to the atmosphere. Overall, the isotope effect on the branching ratio appears to be small.

Our new results have established the kinetic significance of the minor channel for the OH + ClO reaction. The branching ratio involving the production of HCl was determined to be 7% under stratospheric conditions. Numerous atmospheric modeling studies have proposed that a branching ratio close to 7% would resolve discrepancies between measured and calculated chlorine partitioning in the upper stratosphere and help to resolve some of the discrepancies between measured and calculated O<sub>3</sub> concentrations, especially near 40 km. Our results should help to improve modeling of O<sub>3</sub> levels in the upper stratosphere by placing more stringent constraints on the partitioning of stratospheric chlorine.

We have now completed the OH + ClO project. Dr. Matthias Oltzman of the University of Halle-Wittenberg in Germany is a collaborator on this work; he carried out detailed multichannel RRKM calculations, which demonstrate that the theoretical predictions are in very good agreement with the experimental results. We are preparing a manuscript that will be submitted for publication in the near future.

### Photolysis quantum yield measurements with the CIMS technique

We have continued developing a technique to measure quantum yields for the decomposition of chemical species at wavelengths for which the absorption cross sections are very small. The technique relies on measurements of trace amounts of product species in the presence of large amounts of precursor compounds; it employs a Xenon arc lamp as the photolytic light source and chemical ionization mass spectrometry as the analytical tool.

The first system we have investigated is the production of O (<sup>1</sup>D) atoms in the photolysis of ozone at wavelengths longer than 320 nm. While the quantum yield decreases by only an order of magnitude between 300 and 330 nm, the overall yield for production of O (<sup>1</sup>D) decreases three orders of magnitude due to the large drop in absorption cross section over that wavelength range [DeMore *et al.*, 1997]. The experiment consisted of measuring NO<sub>2</sub>, which is produced by the reaction of O (<sup>1</sup>D) with excess N<sub>2</sub>O present in the system, and with large excess ozone — the photolytic precursor species. This resulted in a complication in the ionization scheme we were originally employing, since the abundance of O<sub>3</sub> depleted the primary reactant ion (SF<sub>6</sub><sup>-</sup>). Hence, we tested several alternative ionization schemes such as positive ionization by the primary ion, O<sub>2</sub><sup>+</sup> and ionization involving O<sub>3</sub><sup>-</sup>.

The primary ion O<sub>2</sub><sup>+</sup> did ionize NO<sub>2</sub> to make NO<sub>2</sub><sup>+</sup>, and we observed the first evidence of O(<sup>1</sup>D) production from the photolysis of O<sub>3</sub> at long wavelengths using this ionization scheme. However, positive ionization proved to be difficult to work with, mainly due to clustering with the ions. The other ionization scheme that was implemented utilized the O<sub>3</sub> that was already present in excess. The initial ion, SF<sub>6</sub><sup>-</sup>, ionized the O<sub>3</sub> to make O<sub>3</sub><sup>-</sup>, which in turn reacted with NO<sub>2</sub> to produce NO<sub>3</sub><sup>-</sup>. This scheme offered a high sensitivity to NO<sub>2</sub> as well as the simplicity in using the excess O<sub>3</sub> in the ionization system. This ionization scheme was eventually selected for our measurement of the O (<sup>1</sup>D) quantum yield.

The quantum yields measurements were carried out relative to the values in the well-known region of the spectrum around 300 - 305 nm. Although the scatter in the measurements was significant, we clearly observed production of O (<sup>1</sup>D) between 320 and 330 nm. We measured

an overall trend of the falloff of the quantum yield with increasing wavelength in agreement with recent literature reports, demonstrating that the CIMS photolysis system possesses a large dynamic range and is capable of detecting very small product yields. Future work will focus on the reduction of the experimental scatter; for example, using a tunable laser as a photolytic light source instead of a relatively weak lamp would yield significantly larger signals.

Currently, the chemical ionization mass spectrometer (CIMS) photolysis system is being utilized to investigate the pressure dependence of the photodissociation of  $\text{Cl}_2\text{O}$ . A better understanding of the photodissociation process for this species will aid in the understanding of the photodissociation of similar molecules that are important in the stratosphere. The question remains as to the possibility of quantum yields for photodissociation smaller than unity for small molecules with a continuum spectrum, as has been suggested by Nickolaisen *et al.* [1996].

Our preliminary work has focused on devising and implementing titration and chemical ionization schemes suitable for use with the large abundance of  $\text{Cl}_2\text{O}$ , which is necessary for this experiment. The Cl-atoms — produced from the dissociation of  $\text{Cl}_2\text{O}$  — react with an excess of ethane to make HCl, which can then be ionized and detected. The primary ion being used is  $\text{NO}_3^-$ . Because  $\text{NO}_3$  has such a large electron affinity, it is not depleted by the large abundance of  $\text{Cl}_2\text{O}$ . However, the HCl can still be detected because it clusters with the  $\text{NO}_3^-$  ion to form  $\text{NO}_3^-\cdot\text{HCl}$ . In our initial test of the titration and ionization schemes, we have detected Cl-atoms produced in the photodissociation of  $\text{Cl}_2$  as  $\text{NO}_3^-\cdot\text{HCl}$ . The sensitivity available with this scheme appears to be sufficient for the study of  $\text{Cl}_2\text{O}$  photolysis at the wavelengths and pressures of interest.

### **Statement of Work for the Third Year of the Project:**

1. The rate constant for the  $\text{HO}_2 + \text{ClO}$  reaction will be measured over a range of temperatures using the flow tube – CIMS apparatus. The experimental approach will be similar to that employed for our study of the  $\text{OH} + \text{ClO}$  reaction.
2. The measurement of the quantum yield for photodissociation of  $\text{Cl}_2\text{O}$  will be completed.

3. The quantum yields for photodissociation of ClOOCl will be investigated using the flow tube – CIMS technique.
4. The effect of water vapor on various reactions of the HO<sub>2</sub> radical will be investigated using the flow tube – CIMS approach.

## References:

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## Budget For the Third Year\*

Year 3

### 1. Direct Labor

#### **(a) Salaries**

1 Postdoctoral Research Associate (100% of 12 mos.)	33,000
2 Graduate Research Assistants (100%, 12 mos.) -no fringe benefits	24,000
1 Undergraduate Research Assistant (summer) - no fringe benefits	3,000
1 Project Support Staff (15%, 12 mos.)	<u>6,140</u>
<b>Sub-total Salaries</b>	66,140

#### **(b) Fringe Benefits**

Employee Benefits (26.7% of salaries)	10,450
Vacation Accrual (11% of salaries)	<u>4,306</u>
<b>Sub-total Fringe Benefits</b>	14,756

**Direct Labor (salaries, fringe benefits)** 80,896

### 2. Other Direct Costs

#### **(a) Travel** 2,800

National professional meeting for 2 persons @ \$1400/person  
Airfare - 600; subsistence - 500; misc. - 300

#### **(b) Materials and Services** 10,000

Liquid Nitrogen, Chemicals, Glassware,  
Hardware, Glass and Machine Shop Service

#### **(c) Publications** 1,000

#### **(d) Tuition for Graduate RAs (no OH)** 45,000

**Total Other Direct Costs** 58,800

### 3. Total Direct Costs 139,696

### 4. Modified Total Direct Costs (MTDC) 94,696

### 5. Indirect Costs (63.5% of MTDC) 60,132

**TOTAL ESTIMATED COSTS** \$199,828

**\* Budget Notes:**

The amount of the total estimated costs is the same as the one submitted previously with the three-year proposal and approved for the multi-year grant by NASA Headquarters. The budget items are similar except with the following changes:

- (a) Salary: MIT fully supports the salary of Institute Professor Mario J. Molina (PI); therefore we have applied the salary originally allocated for the PI (1 summer month) to support the second graduate RA at 100% instead of 50% in the original budget.
- (b) Fringe benefits and indirect costs are calculated based on the new guidelines from MIT Office of Sponsored Program and approved by the Office of Naval Research.
- (c) Travel: We are requesting travel support for two persons (PI and a student) to attend one national professional meeting; the estimated cost is \$2,800 (original budget is \$1500 for only one person).

# BUDGET SUMMARY

Year 3                      From                      1/1/99                      to                      12/31/99

	RECIPIENT'S COSTS		NASA USE ONLY	
	A		B	C
1. Direct Labor (salaries, wages, and fringe benefits)	80,896			
2. Other Direct Costs:				
a. Subcontracts	0			
b. Consultants	0			
c. Equipment	0			
d. Supplies (M&S)	10,000			
e. Travel	2,800			
f. Other (Publication)	1,000			
3. Indirect Costs	60,132			
4. Other Applicable Costs (tuition RAs)	45,000			
5. SUBTOTAL - Estimated Costs	199,828			
6. Less Proposed Costs Sharing (if any)	0			
7. Carryover Funds (if any)				
a. Anticipated amount				
b. Amount used to reduce budget	0			
8. TOTAL ESTIMATED COST	199,828			XXXXXXXXXXXXX
APPROVED BUDGET	XXXXXXXXXXXXX		XXXXXXXXXXXXX	

## Instructions

1. Provide a complete budget summary sheet for year one and separate estimates for each subsequent year.
2. Recipient's estimated costs should be entered in Column A. Columns B and C are for NASA use only. Column C represents the approved grant budget.
3. Provide as attachments detailed computations of estimates in each cost category with narratives required to fully explain proposed costs. See Page No. 2, Attachment C (over).